Materials Science and Engineering C 57 (2015) 265–271

Contents lists available at ScienceDirect

Materials Science and Engineering C

journal homepage: www.elsevier.com/locate/msec

Design of a novel coumarin-based multifunctional fluorescent probe for $Zn^{2+}/Cu^{2+}/S^{2-}$ in aqueous solution

Jing-can Qin, Zheng-yin Yang *

College of Chemistry and Chemical Engineering, State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, PR China

ARTICLE INFO

Article history:
Received 14 December 2014
Received in revised form 13 July 2015
Accepted 31 July 2015
Available online 4 August 2015

Keywords:
Multifunctional
Fluorescent sensor
Zinc
Copper
Sulfide

ABSTRACT

A multifunctional fluorescent chemosensor 7-(diethylamino)-coumarin-3-carbaldehyde-(2'-methylquinoline-4'-formyl) hydrazone (HL) has been designed and synthesized. The sensor shows significant fluorescence enhancement in the presence of Zn^{2+}, which might be mainly due to the restricted –C=N isomerization process. In contrast, the fluorescence of the sensor is quenched by Cu^{2+} attributed to the inherent paramagnetic species. More interestingly, the 'in situ' prepared L–Cu exhibits a selective response to S^{2-} based on reversible formation–separation of complex L–Cu and CuS.

1. Introduction

As is well-known, zinc and copper, two of the most abundant transition metal ion, are widely dispersed and used in the environment around us [1–3]. They play some critical roles in a variety of biological process such as gene transcription, regulation of metalloenzymes, and neural signal transmission in the human body [4–8]. Hence, a quantity of Zn^{2+} and Cu^{2+} is essential and beneficial for our good health. Whereas, overloading conditions, they exhibit toxicity in that they cause neurodegenerative diseases such as Alzheimer's, Parkinson's [9–12], Menkes and familial amyotropic lateral sclerosis [13–15]. And in general, the normal Zn^{2+} content of blood plasma is 12 to 16 mM in the body [16], the maximum amount of Cu^{2+} in drinking water is limited to 20 μM which is restricted by the Environmental Protection Agency (EPA) of the U.S. regulations [17–19]. Sulfide, as a traditional toxic anion, has many applicable utilities such as manufacture of sulfur and sulfuric acid, dyes and cosmetics [20–22]. On the other hand, it is exposure to high levels of sulfide that can result in various physiological and biochemical problems including irritation in mucous membranes, unconsciousness, and respiratory paralysis [23]. For these reasons, in order to protect the environment and human health, it is crucial to develop a convenient analytical method for the detection and recognition of excessive amounts of these ions.

Fluorescent probes with operational simplicity, high sensitivity, and inexpensive operational cost have attracted considerable attention [24–26]. However, the simultaneous detection and identification of multiple ions by multifunctional fluorescent probe is still few in number. Compared to single-ion responsive molecular sensors, the multifunctional sensors have been actively developed because of the advantages such as analytical time reduction [27–29]. Coumarin is a kind of compound with great fluorescent intensity, high quantum yield, and is very suitable to act as fluorescent chromophores [30–33]. In addition, Schiff bases are well known to be good ligands which provide an electron-rich environment, which made it easy to bind with metal ions [34–36].

With this in mind, we have designed and synthesized a coumarin-based multifunctional fluorescent probe for Zn^{2+} and Cu^{2+} in aqueous solution (Scheme 1). On one hand, the sensor exhibits a large fluorescence enhancement in the presence of Zn^{2+}. On the other hand, the fluorescence of the sensor demonstrates obvious fluorescence quenching in the presence of Cu^{2+}. Even more surprising, the emission signals of 'in situ' prepared L–Cu can be restored with S^{2-}. Thus, the 'in situ' prepared L–Cu could develop a platform as new sulfide sensor.

2. Experimental

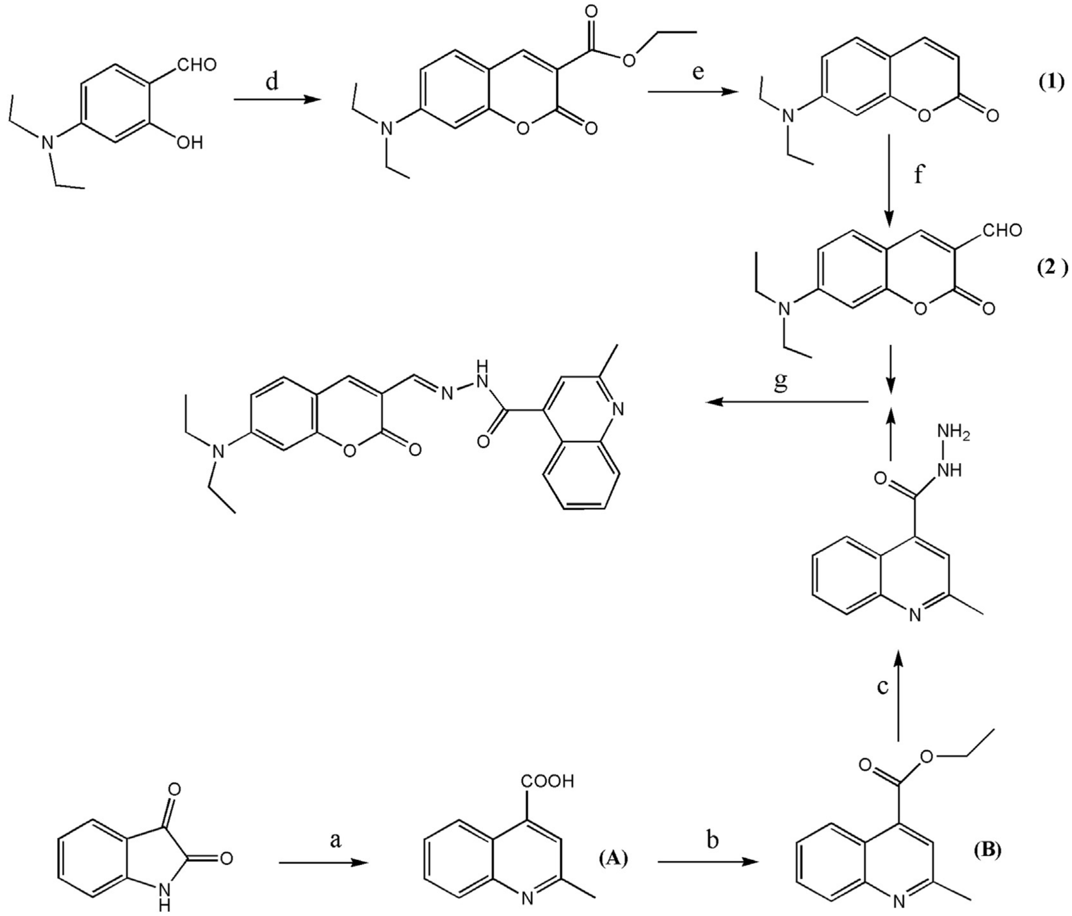
2.1. Apparatus and reagents

Unless mentioned otherwise, all chemicals for synthesis were purchased from commercial suppliers and used without further purification. JNM-ECS 400 MHz instruments using TMS as an internal standard, ESI-MS were determined on a Bruker esquire 6000 spectrometer. UV-Vis absorption spectra were measured on a Perkin Elmer Lambda 35 UV-vis spectrophotometer. Fluorescence spectra were generated on a Hitachi RF-5301 spectrophotometer equipped with quartz cuvettes

---

* Corresponding author.
E-mail address: yangzy@lzu.edu.cn (Z. Yang).

http://dx.doi.org/10.1016/j.msec.2015.07.064



Scheme 1. Reagents and conditions: (a) (i) acetone, aq KOH, reflux, 15 h; (ii) conc HCl; (b) conc H_2SO_4, EtOH, reflux, 18 h; (c) EtOH, $N_2H_4 \cdot H_2O$, 80 °C, 20 h; (d) EtOH, diethylmalonate, piperidine, reflux, 10–12 h. (e) HCl (37%,) and glacial acetic acid;(f) anhydrous DMF, $POCl_3$.

of 1 cm path length. Melting points were determined on a Beijing XT4-100× microscopic melting point apparatus.

Stock solutions of various metal ions (1 mM) were prepared using nitrate salts. Stock solutions of various anions (10 mM) were prepared using sodium salts. A stock solution of HL (1 mM) was prepared. The excitation slit width was 3 nm, the emission slit width was 1.5 nm.

2.2. Synthesis of ethyl 2-methyl quinoline-4-carboxylate [37,38]

A mixture of isatin (6.8 mmol, 1.0 g) and 85% KOH (2.67 g, 47.6 mmol) was heated to 50 °C for 1 h. Then acetone (5 ml, 56.7 mmol) was added dropwise and stirred for 20 h. The reaction mixture was cooled to ambient temperature and acidified to pH 3 by 37% HCl to obtain heavy slurry which was filtered, washed and dried to afford A. Mp: 248–250 °C. H_2SO_4 was added to an ethanol solution (75 ml) of A (3 mmol, 0.56 g) (conc. 3.5 ml). After being refluxed for 24 h, solvent was removed and the residue was partitioned between EtOAc and saturated $NaHCO_3$ solution. The organic layer was washed with water and brine, dried over anhydrous Na_2SO_4, filtered, and condensed to give ethyl 2-methyl quinoline-4-carboxylate. Mp: 71–72 °C, ^{1}H NMR (400 MHz, $CDCl_3$) (Fig. S1): $\delta = 1.47$ (t, J = 7.2 Hz, 3H), 2.82 (s, 3H), 4.51 (q, $J_1 = 7.2$ Hz, $J_2 = 14.0$ Hz, 2H), 7.61 (t, $J = 8.0$ Hz, 1H), 7.76 (t, $J = 8.0$ Hz, 1H), 7.82 (s, 1H), 8.10 (d, $J = 8.4$ Hz, 1H), 8.69 (d, $J = 8.4$ Hz, 1H).

2.3. Synthesis of 2-methyl quinoline-4-carboxylic hydrazide

Hydrazine hydrate (80%, 4 ml) was added dropwise to an ethanol solution (40 ml) of ethyl 2-methyl quinoline-4-carboxylate (5 mmol, 1.015 g) and refluxed under stirring for 20 h. Then the solvent was concentrated under reduced pressure and cooled to room temperature, a white needle crystal was observed. The final product was filtered, dried and recrystallized from ethanol. Mp: 178–179 °C, ^{1}H NMR (400 MHz; $CDCl_3$) (Fig. S2): $\delta = 2.71$ (s, $3H_e$), 4.25 (s, $2H_h$), 7.29 (s, $1H_f$), 7.54 (m, $1H_b$), 7.59 (s, $1H_g$), 7.73 (m, $1H_c$), 8.05 (d, $J = 8.4$ Hz, $1H_d$), 8.14 (d, $J = 8.1$ Hz, $1H_a$).

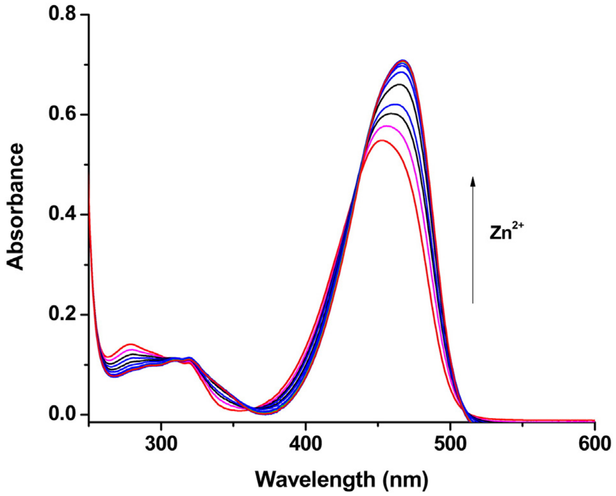


Fig. 1. Absorption spectra of HL (10.0 μM) in ethanol and water (9:1, v/v) upon the addition of Zn^{2+} (0, 2, 4, 6, 8, 9, 10, 11, 12 μM).